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(54) Title: COMPACT REACTOR

(57) Abstract: A reactor assembly comprising a first region for performing an endothermic reaction, a second region for performing an exothermic reaction and the reactor assembly being arranged to transfer heat between the first and second regions, characterised in that the reactor assembly includes a diffusion bonded heat exchanger having two sets of channels formed therein with the first set of channels forming at least part of the first region, the second set of channels forming at least part of the second region and the diffusion bonded heat exchanger being arranged to transfer heat between the two sets of channels.

COMPACT REACTOR

The present invention relates to a reactor assembly having a first region for performing an endothermic reaction and a second region for performing an exothermic reaction and the reactor assembly being arranged to provide good heat conduction between the first and second regions. The reactor assembly is particularly suitable for use as a steam reformer in which the endothermic catalytic conversion of steam and a fuel stream into hydrogen and carbon oxides is performed in the first region and the exothermic combustion of a fuel stream is performed in the second region. Hydrogen produced by a steam reformer is particularly suitable for use in one or more fuel cells to produce electricity.

Conventionally a reactor designed for steam reforming of hydrocarbon fuel comprises a first reaction chamber to perform the catalytic steam reforming reaction within which solid catalyst particles are disposed. The first reaction chamber is in a good heat conducting relationship with a second reaction chamber which may be a furnace surrounding the first reaction chamber to provide heat to the first reaction chamber to make the steam reforming reaction more energetically favourable. Such a reactor is disclosed in US 4203950.

Another type of steam reformer is a Haldor Topsoe Heat Exchange Reformer as described in 'Scale up Study of Heat Exchange Reformer for 5MW Fuel Cell Plant' from the 1992 Fuel Cell Seminar Proceedings, Courtesy Associates Inc., Washington DC, USA. This reformer has a toroidal shaped catalyst bed acting as the first reaction chamber with heat from a burner supplied to the inside and outside of the toroid. The application of heat to both the inside and

outside of the toroidal shaped catalyst bed improves the heat transfer to the first reaction chamber and so also the energy density of the reformer when used to supply hydrogen to a fuel cell.

A further type of steam reformer is an IHI plate reformer as described in EP-A-0430184. This reformer includes a multi-layer unit comprised of parallel plates that are welded together to form a series of chambers. Alternating chambers are used for steam reforming and for combustion which improves the heat transfer between the combustion region and the steam reforming region and so also the energy density of this type of reformer when used with a fuel cell.

However, such reactors are generally large and heavy because of their need to house solid catalyst particles and/or because of their brazed or welded construction. The reactors are particularly unsuitable for use in mobile applications such as to provide hydrogen to one or more fuel cells in a vehicle. Furthermore it is desirable to improve the heat transfer between the first and second regions of such reactors.

According to a first aspect of the present invention there is provided a reactor assembly comprising a first region for performing an endothermic reaction, a second region for performing an exothermic reaction and the reactor assembly being arranged to transfer heat between the first and second regions, wherein the reactor assembly includes a diffusion

bonded heat exchanger having two sets of channels formed therein with the first set of channels forming at least part of the first region, the second set of channels forming at least part of the second region and the diffusion bonded heat exchanger being arranged to transfer heat between the two sets of channels.

A diffusion bonded heat exchanger is very compact and provides very good heat transfer between the first set of channels forming at least part of the first region and the second set of channels forming at least part of the second region. Experimental work has demonstrated that heat fluxes higher than 10 kW/m^2 can be achieved. The good heat transfer enables the reactions in each region to be performed more effectively and low thermal inertia provides faster start-up and better load following characteristics than conventional reactors. Thus the use of a diffusion bonded heat exchanger produces a very compact and very effective reactor.

The first region may for example be arranged to be supplied with steam and fuel gas to perform an endothermic steam reforming reaction. The second region may be arranged to be supplied with fuel to be combusted. When the reactor is used as a steam reformer its compact size and very high heat transfer rate make it particularly suitable for use to produce hydrogen for fuel cell systems for both stationary power plant and in fuel cell systems for mobile applications. Alternatively the first region may be arranged to perform some other reaction such as an endothermic partial oxidation reaction.

Table 1 below shows the energy density of the prior art steam reformers discussed above when used to supply hydrogen to a fuel cell which provides energy, compared to a steam reformer using the diffusion bonded reactor of the present invention. As can be seen the diffusion bonded reactor of the present invention has an energy density which is orders of magnitude better than previous reactors and so a dramatic reduction in reformer volume and weight is achieved for production of the same amount of hydrogen/energy.

Table 1

	Conventional Reformer	Haldor Topsoe Heat Exchange Reformer	IHI Plate Reformer	Reactor of the Present Invention
KW/litre	0.06	0.1	0.3	7-13

At least some of either or both sets of channels may be provided with catalyst to assist the reaction to be performed in those channels. The catalyst is preferably coated onto the inside surface of the channels as a film. Alternatively the catalyst may be provided as particles contained within the channels by for example a mesh at each end of the channels.

An example of a reactor according to the present invention is illustrated in the accompanying drawings in which:

Figure 1 diagrammatically shows a diffusion bonded heat exchanger forming a reactor;

Figure 2 diagrammatically shows another diffusion bonded heat exchanger forming a reactor with the channels in a different arrangement;

Figure 3 illustrates a steam reforming reaction and a combustion reaction performed within the reactor and

Figure 4 is a flow diagram of a reactor used as a steam reformer to supply hydrogen to a fuel cell.

The diffusion bonded heat exchanger 10 illustrated in Figure 1 is a solid body 11 with three opposite pairs of sides 20, 30; 40, 50; 60, 70; with each opposite side being substantially parallel and identical to the other. Two opposite sides 20, 30 have a set of channels or passages 21 passing between them through the body of the heat exchanger 10 (only some of which are shown), for the passage of fluid therethrough. Two other opposite sides 40, 50 have a second set of channels or passages 41 passing between them through the heat exchange body 10 (only some of which are shown), in the example of Figure 1 in an orthogonal direction to the first set of channels 21 also for the passage of fluid therethrough. Each passage 21, 41 passes from one side 20, 40 to the opposite side 30, 50 without coming into fluid communication with channels passing in the orthogonal direction between two other opposite pairs of sides.

The diffusion bonded heat exchanger 10 may be formed by any suitable method as is well known to the skilled man. Formation generally comprises the provision of a number of

plates, some or all of which are provided with suitable channels. The plates are stacked with channels appropriately orientated. The stack is then subjected to appropriate heat and pressure for the plates to be diffusion bonded together to form a solid block with at least two sets of passages therethrough. To produce an equivalent amount of heat exchange between two sets of flow channels, a conventional heat exchanger formed of welded or brazed plates would have to be many times larger and heavier than its diffusion bonded equivalent.

The diffusion bonded heat exchanger offers a very compact design with a surface density of up to $5000 \text{ m}^2/\text{m}^3$. The material used in the reactor depends on several factors such as long term strength (creep resistance), corrosion resistance, catalyst coating characteristics, fabrication limitations and cost. When used as a steam reformer, the reactor will need to handle gases in the temperature range 650°C - 850°C and pressure from 1 bar to about 8 bar. Many metals are suitable for this purpose such as relatively low cost conventional stainless steel, alloyed iron such as iron-chromium alloy which has established catalyst coating characteristics, Ni-based alloys with increased high temperature strength and oxide dispersion strength alloys. Ceramic materials such as alumina may also be used, especially when the reactor is used at high temperatures.

A manifold (not shown) may be positioned over each of the sides 20, 30, 40, 50 to supply fluid to or receive fluid from the channels 21, 41. If the reactor is used as a steam reformer, a first manifold is arranged to supply steam and fuel, preferably fuel gas such as natural gas or

methane to one side 20 containing the first set of channels 21. The fuel and steam is arranged to react in the channels 21 which act as the first reaction region and the products of the reaction pass through the channels 21 to the opposite side 30 of the heat exchanger 10 to be received by a second manifold (not shown). The channels 21 acting as the first reaction region are preferably provided with catalyst to increase the reaction rate as described later.

In a similar manner a third manifold may be arranged to supply fluids to another side 40 of the heat exchanger containing entrances to the second set of channels 41. The fluids delivered by the third manifold are arranged to react within the second set of channels 41 acting as the second reaction region. The products of the reaction in the second region pass through the second set of channels 41 and are received by a fourth manifold positioned over the side 50 of the heat exchanger opposite to the side arranged to receive the third manifold. If the first set of channels 21 is used to perform a steam reforming reaction, the second set of channels is preferably arranged to perform an exothermic reaction such as combustion of fuel, preferably fuel gas such as natural gas or methane. Catalyst may be provided within the second set of channels 41 as described later.

The channels need not necessarily pass between opposite sides of the heat exchanger but could pass between any two parts of the heat exchanger as is convenient. For example the first 21 and second 41 sets of channels may pass through the body 11 of the heat exchanger 10 between different portions 22, 23; 42, 43 of the same side 20; 40 as diagrammatically shown

in Figure 2 or between adjacent sides (not shown). However the channels are arranged, it is preferable that the first 21 and second 41 sets of channels overlap each other or are interleaved for enhanced heat transfer between the endothermic and exothermic regions. Furthermore the heat exchanger 10 may not be a parallelepiped but may be of any shape as is convenient.

Catalyst is preferably deposited directly onto the heat exchange surface of either or both of the sets of channels 21, 41. Catalyst is preferably coated onto the inside surface of either or both of the sets of channels 21, 41 as a film. When catalyst is deposited on both sets of channels 21, 41 the catalysed regions can exchange heat directly with each other.. The preferred method of coating the film is by using a sol-gel as is well known in the art (see for example 'Fundamental Principles of Sol-Gel Technology' by R W Jones published by the Institute of Materials 1989) and which may be applied to the inside surface of the desired channels by established methods such as by being blown through the channels by a stream of air. Alternatively or additionally catalyst may be provided as small particles located within either or both sets of heat reformer channels 21, 41. The catalyst particles may be maintained within the appropriate channels by a mesh at each end.

Figure 3 diagrammatically shows the reactions performed in adjacent channels 21, 41 when the heat exchanger 10 of the reactor is used as a steam reformer. Channels 41 shown coated with a catalyst film 45 receive a stream of fuel, in this case methane which is combusted with air in

the presence of the catalyst 45 and produced heat passes through the body 11 of the heat exchanger 10 to channels 21 in which a steam reforming reaction is performed. Channel 21 receives a fuel stream, in this case methane and water to produce hydrogen in the presence of catalyst film 25. The heat received from surrounding channels 41 promotes the steam reforming reaction increasing hydrogen yield.

Platinum (Pt) and palladium (Pd) are among the most active catalysts for the catalytic combustion of a range of fuels including natural gas. Palladium has been found to have a higher activity for methane combustion. Other noble metals may be used. Rhodium is used, for example in automotive exhaust catalysts while iridium and ruthenium added to catalyst formulations have been found to reduce the tendency of the catalyst to sinter and deactivate. Noble metal combustion catalysts exhibit high activity. Platinum and palladium based catalysts may operate at temperatures up to 1300°C. The use of the reactor of the present invention as a compact reformer thus does not pose any temperature restrictions on the use of Pd or Pt catalysts, and these are the preferred option.

The catalyst support is also important for the reformer. Traditional pelleted catalysts use supports of alumina or silica to maximise the surface area and give good dispersion of the active metal. The most widely used support is gamma-alumina. If the reformer is to operate for prolonged periods above 700°C, stabilisers may be added to the support to minimise the sintering of the support, brought about by a phase change from gamma to alpha alumina.

Stabilisers such as CeO_2 or CsO_2 may be added to the support, to raise the temperature at which sintering commences. In the present case un-doped gamma alumina has been used.

For the present example a thin film Pd/alumina combustion catalyst was prepared as follows. A palladium nitrate/alumina sol was made up by dissolving palladium nitrate hydrate (0.225g) in 50 ml water. To 25 ml of this cloudy brown solution was added 1 ml of 70% nitric acid (1.45g). A further 25 ml of water was added to this solution. Condea alumina (10g) was then added slowly with continuous rapid stirring. The final 2g of alumina was added with a further 12 ml of water. The sol therefore consisted of Pd 0.048g; NO_3 1.0g; Al_2O_3 8g and water 64g. This corresponds to 0.6% Pd on alumina catalyst after complete calcination.

For a reactor with 1.5 mm diameter channels, approx. 1 ml of sol was forced through the reactor with a gentle stream of air. Most of the sol came out leaving a thin film adhered to the reactor wall. This was dried in a stream of air for 1.5 hours before the coating procedure was repeated. The reactor was then further dried at 100°C before calcining at 500°C in air. For a reactor with 2.5 mm diameter channels, the sol was first thinned with 25% water. A 2ml aliquot of this was then blown through the reactor with a gentle downward air stream with the reactor vertical. The reactor was then placed in a horizontal furnace and the temperature gradually increased to 500°C over 4 hours with air flowing therethrough. The reactor was then cooled overnight and the procedure repeated to give a second coat of catalyst.

Nickel has become the most widely used catalyst metal in industry for the steam reforming of hydrocarbons. Other metals such as Co, Ru, Rh, Pd, Pt, Ir may be used but are generally avoided on cost grounds, despite the fact that their intrinsic catalytic activity may be higher, and that they may be less active in promoting carbon forming reactions. In our tests we therefore used Ni catalysts and Ru catalysts that were prepared and applied using a sol-gel method. Ru was used because of its good resistance to sulphur and carbon deposition.

Several catalysts were prepared using nickel or ruthenium as the active metal. These metals were added to the alumina support by the addition of metal salt dissolved in water to give the desired metal/alumina proportion. The active metal concentration in the catalyst prior to use was therefore known. The addition of nickel salt caused gelling of the suspension, i.e. more viscous and thixotropic. This made the initial nickel catalysts poor for coating as the calcined sol tended to flake off. The extent of this gelling increased with the quantity of nickel salt added to the dispersed alumina. Therefore nickel salt was added only until the sol showed significant signs of gelling. The resulting mixture gave an acceptable coat thickness of around 3 microns per dip and did not flake. The extent of gelling on the addition of ruthenium salt was much less significant and the viscosity of the mixed sol-gel differed little from the initial dispersed alumina.

The principal effect in the reactor 10 is that of reaction rates which is in itself influenced by the residence time. The residence time within each channel 21, 41 of the heat exchanger 10 is

influenced primarily by its diameter. Experimentation examined the effect of changing the channel dimensions on the temperature profile. A selection of results is presented in Table 2.

Table 2 below shows that the temperature drops by over 200°C along the reformer channels 21 if little combustion is occurring. By increasing the residence time in the combustion channels 41 compared to the reforming channel, the temperature drop is reduced and the conversion of the fuel increases. The cross-sectional area of the combustion channels 41 is preferably larger than that of the reforming channels 21. The cross-sectional area of the combustion channels 41 may be twice, five times or even ten times that of the reforming channels 21. When using the reactor with some other catalysts it may be desirable for the cross-sectional area of the combustion channels 41 to be smaller than that of the reforming channels 21. The cross-sectional area of the combustion channels 41 may be half, a fifth or even a tenth of that of the reforming channels 21. The diameter of the combustion channel 41 is preferably between 10 and 30 mm and the reforming channel diameter is preferably between 1 and 3 mm. The channels 21, 41 may have an aspect ratio within the range of substantially 1 to 10 and may have a substantially circular cross-section.

It must be remembered that the combustion reaction releases more heat per mole reacted than the reforming reaction absorbs, which could lead to the initial assumption that there is danger of thermal runaway. This work has shown, however, that there is likely to be a self

dampening effect in the reformer, with the rate of the reforming reaction increasing more rapidly with temperature than does the combustion reaction.

It has also been found to be preferable to preheat the combustion air to enhance the heat produced by combustion.

Table 2. Results from Reformer experiments.

Input data					
Combustion conditions:	Inlet temperature	783°C			
	Excess air	100%			
Reforming conditions:	Inlet temperature	760°C			
	Steam/carbon ratio	4			
Combustion channel diameter (mm)	2.8	10.0	20.0	6.0	6.0
Reforming channel diameter (mm)	1.7	1.7	1.7	1.0	0.5
Results					
Combustion exit temperature (°C)	546.0	560.0	609.0	638.0	730.0
Reforming exit temperature (°C)	541.0	555.0	602.0	631.0	723.0
Heat load (W)	1.3	1.6	2.7	1.0	0.6
Combustion conversion (%)	0.3	3.9	16.3	2.0	2.7
Reforming conversion (%)	37.0	38.7	45.0	23.6	9.5

The influence of residence time on temperature leads to a method of controlling the temperature of the reactor. That is by controlling the flow of fuel and oxidant to the combustion side, for example by using suitable valves, it is possible to control the heat released to the reformer and thereby control the conversion of reforming. The performance of the reformer can thus be controlled by applying flow controls to the combustion inlet.

The Tables 3 and 4 below show the operating conditions for the reactor of the present invention when used as a steam reformer to provide sufficient hydrogen for a 200 kW fuel cell system. For a typical system efficiency this requires a natural gas feed rate of 1.8 kmol/h on the reforming side and 0.4 kmol/h on the combustion side. Based on these figures, the weight and volume of the reformer is very low, especially in comparison with other reformers as shown in the introduction.

Table 3 - Operating Conditions for Reformer

	Reforming side	Combustion side
Temperature (°C)	750	770
Pressure (bar a)	6	1.3
Natural gas feed rate (kmol/h)	1.8	0.4
Steam feed rate (kmol/h)	5.4	N/A
Air feed rate (kmol/h)	N/A	4.1
Total feed rate (kmol/h)	7.2	4.5

Table 4 - Weight & Volume of Compact Reformer Design

	Weight (kg)		Volume (litre)	
	/kWe	/200 kWe	/kWe	/200 kWe
Diffusion bonded plate fin heat exchanger compact reformer	0.38	75	0.12	24
Diffusion bonded printed circuit heat exchanger compact reformer	0.95	190	0.11	22

An example of the reactor used as a reformer to supply hydrogen to a fuel cell is shown in Figure 4. Reforming of fuel gas external to a fuel cell stack is a fundamental requirement for all fuel cell systems employing low temperature stacks such as the Solid Polymer Fuel Cell (SPFC), otherwise known as the Proton Exchange Membrane (PEM) fuel cell, the Alkaline Fuel Cell (AFC) and the Phosphoric Acid Fuel Cell (PAFC).

An example of a process design for an SPFC fuel cell system employing a reformer of the present invention is shown in Figure 4. In this example, the reformer 100 is arranged to operate at 750°C and in the combustion section 41 air supplied through inlet 101 is set at 100% excess (i.e. 2 x stoichiometric). The reformer 100 is assumed to be a co-current flow design and air is pre-heated to above the combustion light-off temperature by exchanging heat from a heat exchanger 103 through which gases produced by combustion in the reformer 100 pass via outlet 102. Fuel gas, in this case natural gas, is supplied to reformer 100 via inlet 104 to be combusted with air from inlet 101.

Steam is raised from a water supply inlet 105 which passes through and takes heat from gases leaving the reforming section 21 of the reformer 100 via a heat exchanger 106. The water is combined with fuel gas, in this case natural gas from inlet 107 and which optionally passes through a desulphurisation vessel 108. The fuel gas/steam mixture is supplied to the

reforming channels 21 of the reformer 100 by conduit 109. Hydrogen produced in the reformer 100 is supplied via conduit 110 to a fuel cell (not shown).

The results of studies conducted with the reformer of the present invention supplying hydrogen for a fuel cell showed that sufficient heat is available in the scheme at a combustion excess air rate of 10%. However, no matter how good the heat recovery system is, increasing the excess air rate will increase the flow of hot exhaust leaving the system. This greater hot exhaust flow increases the combustion fuel requirement and hence decreases the overall efficiency.

In general, the greater the preheat obtained on the combustion air, the less combustion fuel will be required, so increasing the efficiency. The preheat possible in the scheme depends on how the heat integration is performed. Studies have shown that preheat temperatures in excess of 700°C are possible with the heat available from elsewhere in the system such as using the heat from the combustion exhaust gases from the reformer 100 in outlet 102 for heat exchange with the input air. Preferably a combustor 111 is used to further heat the combustion exhaust gases in outlet 102.

Many modifications may be made to the example disclosed above whilst still falling within the scope of the invention. For example each set of channels 21, 41 in the diffusion bonded heat exchanger could comprise one or more channels. These channels could pass back and forth

within the heat exchange body 11 to increase the heat exchange effect. Furthermore, catalyst may be provided as a film on the inside surface of one set of channels and provided as particles in the other set of channels.

CLAIMS

1. A reactor assembly comprising a first region for performing an endothermic reaction, a second region for performing an exothermic reaction and the reactor assembly being arranged to transfer heat between the first and second regions;

characterised in that the reactor assembly includes a diffusion bonded heat exchanger having two sets of channels formed therein with the first set of channels forming at least part of the first region, the second set of channels forming at least part of the second region and the diffusion bonded heat exchanger being arranged to transfer heat between the two sets of channels.

2. A reactor according to claim 1, wherein the first and second regions are interleaved with each other.

3. A reactor according to claim 1 or claim 2, wherein at least some of either or both sets of channels is provided with catalyst.

4. A reactor according to claim 3, wherein the catalyst is provided as particles contained within at least some of either or both sets of channels.

5. A reactor according to claim 3, wherein the catalyst is provided directly onto the heat exchange surface of either or both sets of channels.
6. A reactor according to claim 3, wherein the catalyst is provided as a film on the inside surface of at least some of either or both sets of channels.
7. A reactor according to any of claims 3 to 6, wherein a platinum containing catalyst is provided in at least some of the first set of channels.
8. A reactor according to any of claims 3 to 6, wherein a palladium containing catalyst is provided in at least some of the first set of channels.
9. A reactor according to any of claims 3 to 8, wherein a nickel containing catalyst is provided in at least some of the second set of channels.
10. A reactor according to any of claims 3 to 8, wherein a ruthenium containing catalyst is provided in at least some of the second set of channels.
11. A reactor according to any of the preceding claims, wherein a fuel stream and water are arranged to be applied to the first set of channels and a fuel stream and oxygen are arranged to be applied to the second set of channels.

12. A reactor according to any of the preceding claims, wherein the cross-sectional area of the second set of channels is larger than the cross-sectional area of the first set of channels.
13. A reactor according to claim 12, wherein the diameter of the majority of the first set of channels is between 1 and 3 mm and the diameter of the majority of the second set of channels is between 10 and 30 mm.
14. A reactor according to any of the preceding claims, wherein the cross-sectional area of the second set of channels is smaller than the cross-sectional area of the first set of channels.
15. A reactor according to claim 14, wherein the diameter of the majority of the first set of channels is between 10 and 30 mm and the diameter of the majority of the second set of channels is between 1 and 3 mm.
16. A reactor according to claim 9, including a fuel cell arranged to receive hydrogen produced from the first set of channels.
17. A reactor substantially as hereinbefore described with reference to the accompanying drawings.

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FIG. 1.

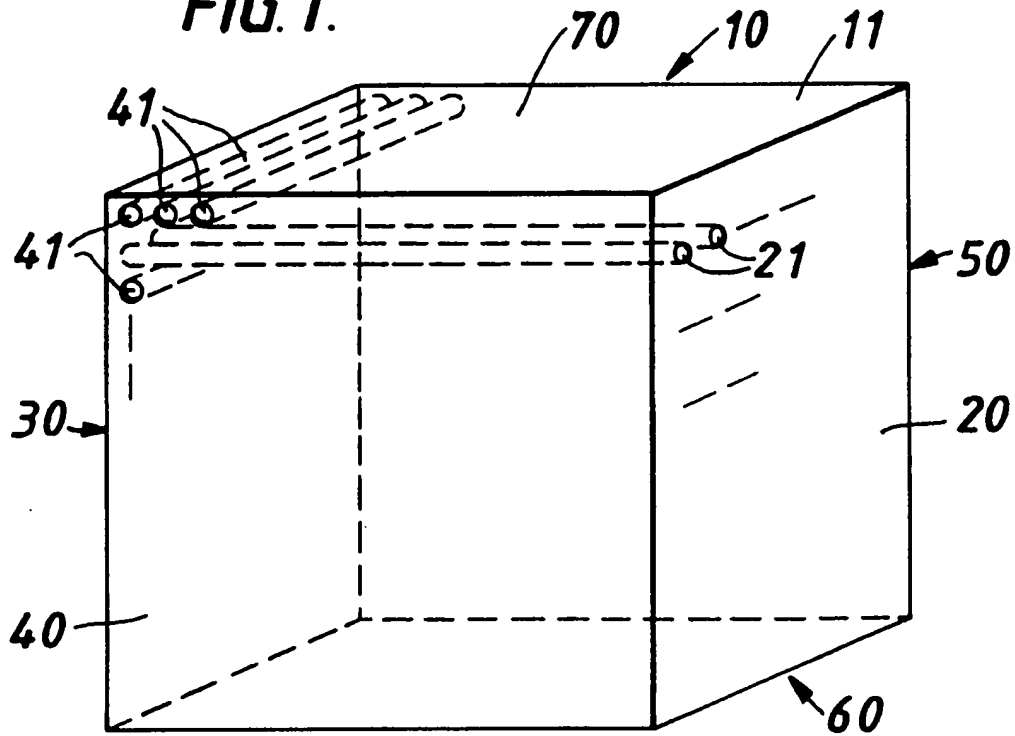
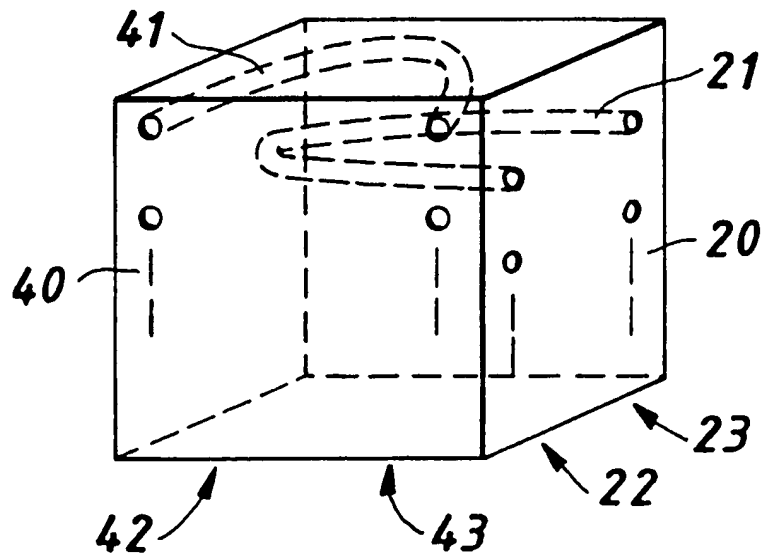
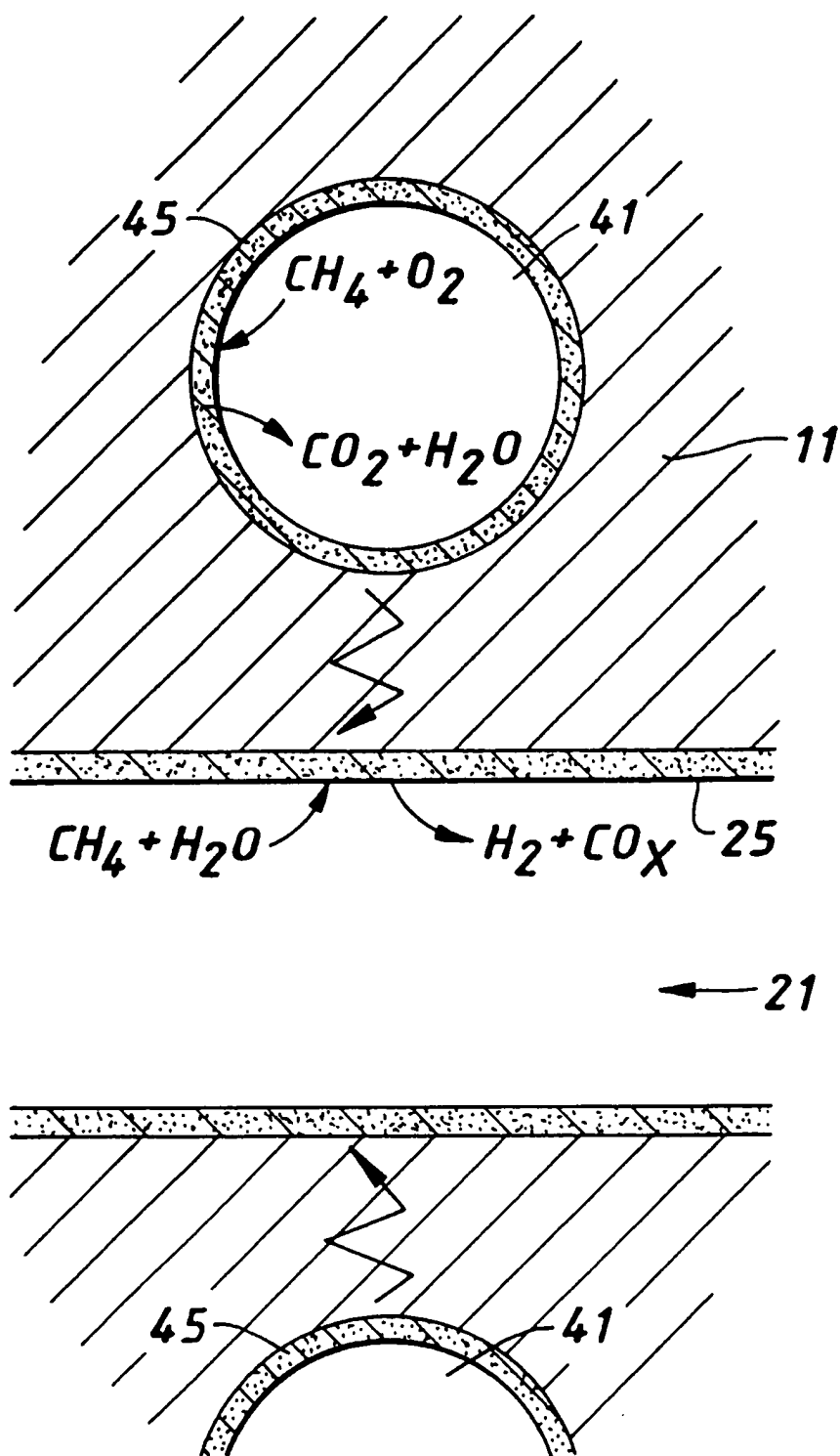


FIG. 2.



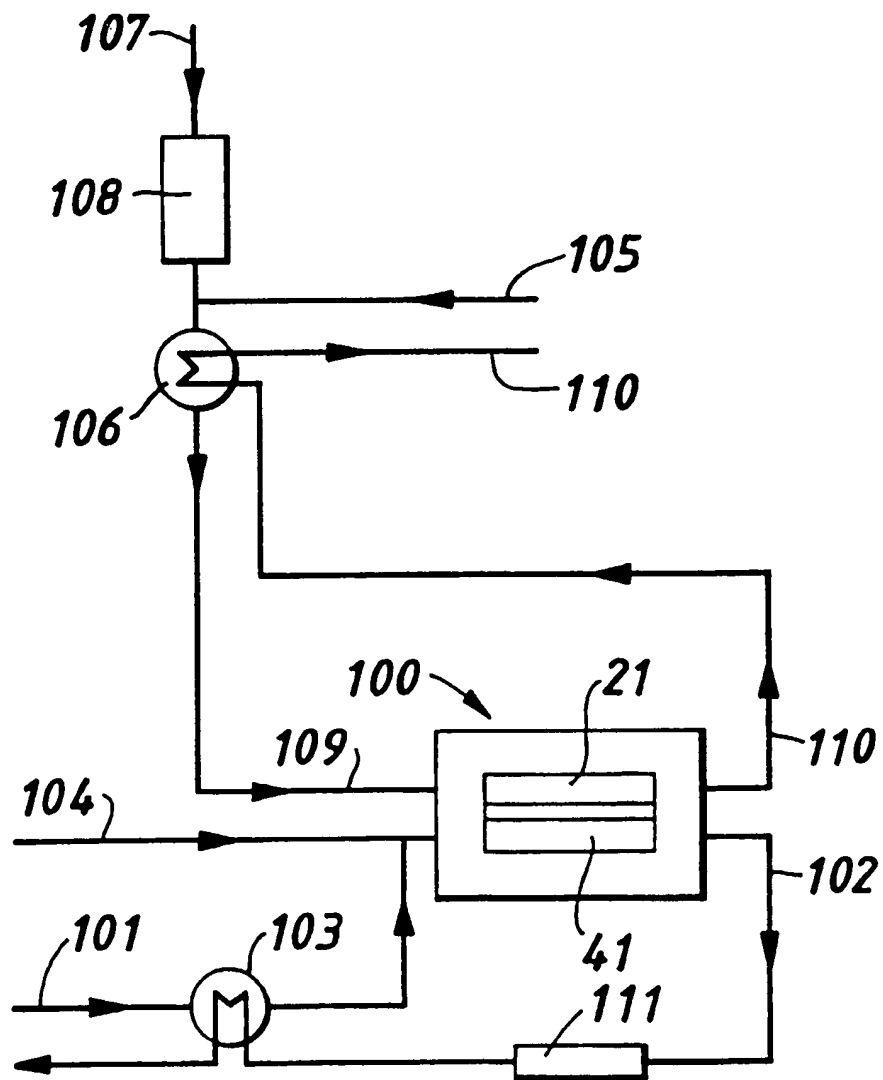
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FIG. 3.



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FIG. 4.



INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B3/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 504 447 A (SPURRIER FRANCIS R ET AL) 12 March 1985 (1985-03-12) claim 1	1
A	EP 0 305 203 A (TOPSOE HALDOR AS) 1 March 1989 (1989-03-01) claim 1	1
A	EP 0 430 184 A (ISHIKAWAJIMA HARIMA HEAVY IND) 5 June 1991 (1991-06-05) cited in the application claim 1	1
A	EP 0 578 218 A (AIR PROD & CHEM) 12 January 1994 (1994-01-12) claim 1	1
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Clement, J-P

INTERNATIONAL SEARCH REPORT

Int. Patent Application No
PCT/GB 00/02887

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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